

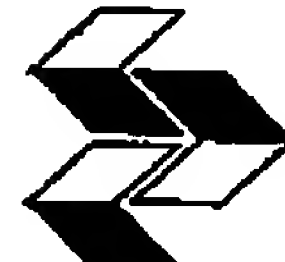
## **ATTACHMENT G**

# **CHLORINE DIOXIDE**

## **Chemistry and Environmental Impact of Oxychlorine Compounds**

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## PREFACE

This book is a description of present knowledge of the chemical basis for technical uses of oxides of chlorine and sodium chlorite. It reviews the principles of the reactivity of oxychlorine derivatives including related analytical methods. Special reference is made implicitly to the direct or indirect environmental implications.

Even though the disinfecting properties of chlorine dioxide were well established in Belgium at the beginning of this century, this oxidant has found more widespread use, especially in the treatment of drinking water and swimming pools, since the 1950s.

It was because of the fact that the cheaper and more traditional chlorine became insufficient, and even at times objectionable, that the use of chlorine dioxide was so extended.

This evolution is still in progress—recently with a new driving force because of the problem of formation of chlorinated derivatives as reaction products from an extensive and general use of chlorine in water and wastewater treatment.

Undoubtedly, the high oxidation capacity of chlorine dioxide in its reactions with dissolved organic compounds, with simultaneous disinfection, without inhibition by ammonia and with less formation of chlorinated organic products, remains the cornerstone to its use in water treatment during this decade.

Oxychlorine derivatives have continued to find extensive applications in air purification and deodorization techniques. Other uses are related to the food processing industry in which a variety of sometimes astonishing applications have been reported.

However, the second basis for a new interest in these old chemicals is their use in pulplog and bleaching techniques for wood pulps, cellulosic fabrics and even synthetic fibers. By substituting chlorine dioxide or chlorite for chlorine to obtain higher bleaching performances and less loss in mechanical strength of the fibers, the environmental impact of chlorinated derivatives is likely to be diminished.

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### COLORIMETRIC AND SPECTROPHOTOMETRIC METHODS

In aqueous solution chlorine may be determined by absorption at 400 m $\mu$ . The molar absorption coefficient of chlorite and chlorine at 400 m $\mu$  is, respectively, 10 and 5% of that of chlorine dioxide. The measure of the absorption at 240, 260 and 400 m $\mu$  generally enables the simultaneous determination of chlorine, chlorite and chlorine dioxide. This technique is not very precise for chlorite. The absorption of chlorite at 260 m $\mu$  follows Beer's law in the range of 3.03 to 5.2 mM.

When interfering salts such as  $\text{Fe}^{+++}$ ,  $\text{Cu}^{++}$ ,  $\text{Ce}^{++++}$ ,  $\text{Sb}^{++++}$  or  $\text{Cr}_2\text{O}_7^{--}$  are present, chlorine dioxide may be determined at 327 to 355 m $\mu$  after extraction by  $\text{CCl}_4$ . The sensitivity is 4 mg  $\text{ClO}_2/\text{l}$ .

Composite mixtures of chlorine dioxide, chlorous acid, chlorite, chlorate and chloride may be analyzed by combined spectrophotometric-titrimetric techniques (32).

Chlorine dioxide is determined spectrophotometrically at 360 m $\mu$ . The molar absorptivity being  $1,100 \pm 50 \text{ l/mole-cm}$ , the interference of chlorite is negligible. The detection limit for chlorine dioxide is on the order of 0.02 mM/l or 1 to 2 mg  $\text{ClO}_2/\text{l}$ . This determination is to be followed by air stripping to remove the chlorine dioxide. At this stage, chlorous acid as well as chlorite are determined spectrophotometrically at 250 to 260 nm. The sensitivity is on the order of 10 mg/l. The total concentration of oxychlorine species remaining after the gas-stripping of  $\text{ClO}_2$  is determined in a strong acid medium (pH  $\leq 1$ ). The overall sensitivity is on the order of 1 to 10 mg/l, expressed as iodide oxidizing species. Finally, chlorite can be titrated by Mohr's technique, preferentially using a mixed indicator of potassium chromate and potassium dichromate. The detection limit is on the order of 5 mg/l for the usual titration techniques.

The classical colored reactions of chlorine obtained by orthotoluidine, helianthins or *p*-aminodimethylaniline enable the determination of  $\text{ClO}_2$ . These visual methods have a maximum sensitivity of about 0.02 mg/l. Quantitative determination in the presence of free chlorine does, however, necessitate a complicated adjustment of reagents. Consequently, the method becomes partially inadequate. Iron interference may be eliminated by precipitation with sodium pyrophosphate. Chlorine interference is minimized by adding oxalic acid or malonic acid before introducing orthotoluidine. Color occurring upon orthotoluidine oxidation is measured by spectrophotometry. However, the instability of absorption may not enable good precision. On the whole, in using these techniques, chlorite is presumed to be absent. If present, the results of these methods are arguable.

Just as does chlorine, chlorine dioxide reacts directly with diethyl-*p*-phenylenediamine, which also provides the same colored reaction with

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iodine and ozone. In a neutral medium, chlorine dioxide reacts directly according to one equivalent. As a variant, one may detect iodine formed by the oxidation of iodide. After oxidation of iodide in an acid medium and subsequent adjustment of the pH to neutrality, five equivalents of chlorine dioxide are revealed. In this way, after two manipulations one may determine mixed chlorine and chlorine dioxide. Among the disadvantages of the method, the instability of the coloration obtained with iodine, which is particularly observed during spectrophotometric measuring, is to be noted. In fact, chlorites are presumed to be absent in the given analytical sequences. If they were present, they would be partly considered as chlorine dioxide. Sensitivity is 0.01 mg/l.

Chlorine dioxide reaction with tyrosine (see Chapter 11) gives colored components, enabling determination by measuring absorption at 490 to 355 m $\mu$ . Chlorine interference is hardly significant in a molar proportion of  $\text{Cl}_2/\text{ClO}_2$  below 2. This interference also may be partially avoided by using ethylamine or malonic acid, so that chlorine in molar proportion to  $\text{ClO}_2$  of 10 to 1 no longer interferes. Typical solutions are molar monoethylamine in an acetic acid-sodium acetate buffer. This solution must be added at a 10% volume ratio to the liquid under analysis. The malonic acid inhibitor of chlorine interferences is a 10% solution added to the water under investigation at a 5% volume rate.

The value of this method depends on the working conditions. The most favorable conditions would be a pH between 4.6 and 4.8 and 3.3 moles of  $\text{ClO}_2$ , more or less, per mole of tyrosine. In this case,  $\text{ClO}_2$  sensitivity is 0.2 mg/l. In the presence of an excessive amount of chlorine dioxide, the reaction continues, forming colorless derivatives.

The useful range of the method is between 0.2 and 1 mg  $\text{ClO}_2/\text{l}$ . If dilution is necessary, the reaction is best operated in vessels cooled to 0°C. To an aliquot of the solution to be analyzed (80 ml) are added, consecutively, 10 ml of a solution of monoethylamine, 6 ml of the tyrosine reagent and 2 ml of buffer solution. After a reaction period of 4 to 10 minutes the coloration is measured at 490 m $\mu$ . Analytical solutions are composed as follows:

*Tyrosine:* disperse 3.2 g in 60 ml normal NaOH and adjust to 1 liter with double-distilled water.

*Monoethylamine:* add 74.5 g of sodium acetate *pro analysi* to 800 ml double-distilled water, and then introduce 62 g of monoethylamine and about 60 ml acetic acid; then adjust the final pH to 4.65 and the volume to 1 liter.

*Buffer solution:* acetate-acetic acid buffer of pH 4.45 containing 0.9 mole of sodium acetate per liter.